Reversible metalation of alkyl and aryl groups by a coordinately unsaturated iron complex

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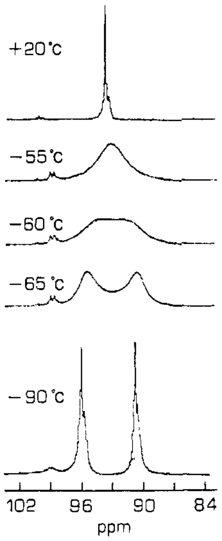


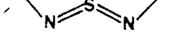
Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $(CO)_5MoP(Ph)_2NSN(Ph)_2PMo(CO)_5$ in acetone-d_6.

of 1.529 (4) and 1.515 (3) Å and P–N bond lengths of 1.732 (3) and 1.706 (3) Å. The longer S–N and P–N bonds are associated with N(1) for which PNS = 117.9 (2)°, cf. P(2)N(2)S = 130.8 (2)°. The NSN angle is 116.0 (2)°. Thus the overall geometry and detailed structural parameters are very similar to those reported for t-$Bu_2P(X)NSN(X)PBu_2$-t (X = S, Se).[14]

Three geometrical isomers are possible for sulfur diimides: cis,cis (**5a**), cis,trans (**5b**), and trans,trans (**5c**). Ab initio MO calculations for MeNSNMe indicate that **5b** is the lowest energy form and provide a value of 16.0 kcal mol^{-1} for the cis,trans to trans,cis interconversion barrier, which is expected to decrease with increasing bulk of the substituents R.[15] This process is thought to occur via the intermediacy of the cis,cis isomer in view of the substantially higher energy of the trans,trans isomer.[15]

5a

5b



5c

As indicated in Figure 2 the $^{31}P\{^1H\}$ NMR spectrum of **4a** in acetone-d_6 at −90 °C shows two equally intense singlets at +96.0 and +90.5 ppm consistent with the existence of the cis,trans isomer in solution at this temperature.[16] When the temperature of the solution is gradually raised, these two signals broaden and collapse until at +20 °C a single, sharp singlet is observed at +93.7 ppm. The reverse of these changes is observed when the solution is cooled again to −90 °C. These observations are consistent with a rapid cis,trans to trans,cis interconversion. The coalescence temperature is −60 °C, which corresponds to an interconversion barrier of 9.4 ± 0.2 kcal mol^{-1}[17] consistent with the prediction of ab initio MO calculations (vide supra).[15] By contrast, no indication of nonequivalence of the two phosphorus substituents in solution was observed for t-$Bu_2P(X)NSN(X)PBu_2$-t (X = S, Se) at −80 °C in CD_2Cl_2[14] or for **2** (R = t-Bu) at −100 °C in CD_2Cl_2.[18,19]

Heterocumulenes of the type RNSO and RNSNR (R = alkyl, aryl) form a variety of mono- and binuclear complexes with organometallic substrates, which may involve M—N, M—S, or M—π-N═S bonding.[20] The preparation of **3a**, the first metal complex of **1**, provides an opportunity to explore the coordination chemistry of this interesting ligand. The extension of the preparative routes described herein to the synthesis of complexes of $RP(NSO)_2$ and $P(NSO)_3$ (and the corresponding sulfur diimides) is another intriguing prospect, which is being pursued.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support in the form of an operating grant (T.C.) and an infrastructure grant for the X-ray structural service. We also thank Dr. K. A. Kerr for the use of the X-ray diffractometer.

Registry No. **3a**, 100815-28-9; **4a**, 100815-29-0; **5b**, 84878-03-5; $(CO)_5Mo(Ph_2PCl)$, 23581-74-0.

Supplementary Material Available: Listings of positional and thermal parameters, all bond distances and bond angles, and observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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[14] Herberhold, M.; Ehrenreich, W.; Gieren, A.; Betz, H; Hubner, T. *Chem. Ber.* **1985**, *118*, 1476. For example, the corresponding data for t-$Bu_2P(S)NSN(S)PBu_2$-t are d(S–N) = 1.527 (1) and 1.513 (1) Å, d(P–N) = 1.702 (1) and 1.697 (1) Å, PN(1)S = 118.4 (1)°, PN(2)S = 136.4 (1)°, and NSN = 116.9 (1)°.

[15] Raghavachari, K.; Haddon, R. C. *J. Phys. Chem.* **1983**, *87*, 1308.

[16] The alternative explanation of the ^{31}P NMR spectrum is that *equal amounts* of the isomers **5a** and **5c** are present at −90 °C. This is very unlikely in view of the steric repulsions between bulky R groups in **5a** and the high energy calculated for **5c** (R = Me).[15]

[17] Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

[18] Herberhold, M.; Ehrenreich, W.; Guldner, K. *Chem. Ber.* **1984**, *117*, 1999.

[19] The structure of **2** (R = Bu-t) in the solid state is unknown, but IR data suggest the existence of two isomers.[2] However, the corresponding arsenic compound has been shown by X-ray crystallography to adopt a cis,cis configuration. Gieren, A.; Betz, H.; Hubner, T.; Lamm, V.; Herberhold, M.; Guldner, K. *Z. Anorg. Allg. Chem.* **1984**, *513*, 160.

[20] Vrieze, K.; van Koten, G. *J. R. Neth. Chem. Soc.* **1980**, *99*, 145.

Reversible Metalation of Alkyl and Aryl Groups by a Coordinatively Unsaturated Iron Complex

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Summary: The coordinatively unsaturated iron(0) species $Fe(DEPE)_2$ [DEPE = 1,2-bis(diethylphosphino)ethane] was generated, and its reactions with C–H bonds in alkyl groups and arenes were investigated.

Recently, a number of workers have reported the reaction of alkyl C–H bonds with complexed transition metals including iridium,[1] rhodium,[2] rhenium,[3] and tungsten.[4] In each of the reported cases, the reactive metal species has been coordinatively unsaturated (formally electron deficient) and hence potentially electrophilic. In the absence of better sources of electrons, an accessible C–H bond can

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[1] Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190–1. Bergman, R. G.; Janowicz, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 352–4. Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121–2.

[2] Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562–3.

[3] Gault, Y.; Felkin, H.; Fillebeen-Khan, T.; Holmes-Smith, R.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 1279–82.

[4] Berry, M.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, *12*, 1950–8. Green, M. L. H. *Pure Appl. Chem.* **1984**, *56*, 47–58 and references therein.

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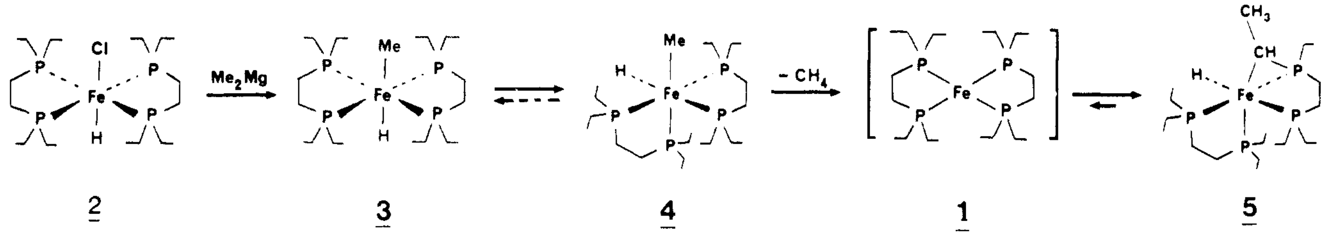
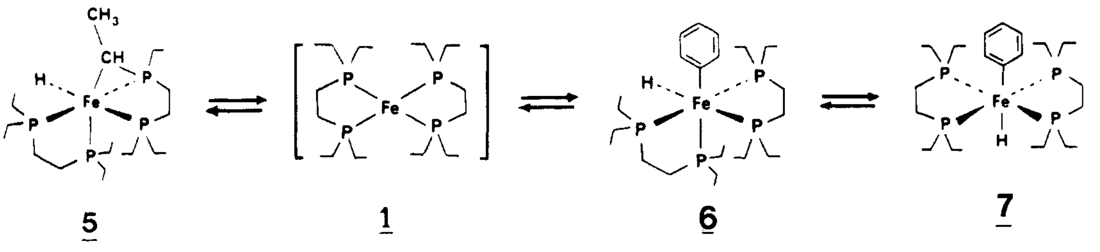
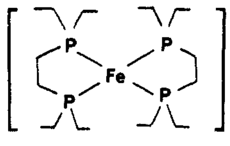
Scheme I



Scheme II



be thought to satisfy the electron deficiency of the metal in an oxidative addition reaction, leading to alkyl or aryl metal hydrides. We report here a series of *reversible* inter- and intramolecular alkylation and arylation reactions which presumably proceed via the coordinatively unsaturated iron(0) species Fe(DEPE)$_2$ (1) [DEPE = 1,2-bis(diethylphosphino)ethane].



1

On addition of excess dimethylmagnesium[5] to a solution of the hydrochloride 2[6] at low temperature (<230 K), the trans methyl hydride 3 is formed quantitatively[7,8] (Figure 1a). On warming the solution above 240 K, 3 isomerizes to the cis isomer 4[9] (Figure 1b) which rapidly eliminates methane. In inert solvents (THF, pentane) the cyclometalated compound 5 is formed cleanly (Figure 1c), and this would arise by the oxidative addition of the coordinatively unsaturated iron atom in 1 to a C–H bond of a methylene group of one of the DEPE ethyl substituents (Scheme I).

The structure of 5 was established by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy.[10] The ^{31}P NMR spectrum of 5 (THF-d_8 solution, 298 K) shows four coupled phosphorus nuclei at δ 91.11, 87.28, 81.44, and 50.83. The resonance to highest field is attributed to the phosphorus in the three-membered metallocyclic ring. Apart from other ligand resonances, the ^{13}C NMR spectrum (THF-d_8 solution; 273 K) shows the presence of one methine carbon at extreme high field (δ(^{13}C) −20.97 ($^{1}J_{\mathrm{CH}}$ = 142 Hz)) assigned to the resonance of the carbon in the three-membered metallocyclic ring. In the ^{1}H NMR spectrum (THF-d_8 solution; 298 K), the iron-bound hydride resonates at δ −15.59 and shows coupling to four distinct phosphorus nuclei. A one-proton signal at δ −0.88 is assigned to the single hydrogen on the three-membered metallocyclic ring, and irradiation of the adjacent CH$_3$ group (δ 1.24) resolves coupling between this proton and the various phosphorus nuclei in the molecule.

When a solution of 5 was treated with D$_2$O/D$_2$SO$_4$ and the liberated ligand was isolated, the deuterium NMR spectrum of the ligand showed a single resonance consistent with deuterium incorporation only at a methylene position of an ethyl group in a DEPE ligand. When stirred under a hydrogen atmosphere, 5 affords the corresponding cis dihydride.[11]

On addition of benzene to 5, at 250 K, the cis phenyl hydride 6 is formed.[12] At higher temperatures, 6 isomerizes to the trans isomer 7 (Scheme II).[13] The ratio of 5:6:7 which coexist in solution varies (reversibly) with temperature, concentration, and solvent composition. At 300 K, the ratios are 33:28:39 (parts d and e of Figure 1).

Using hexadeuteriobenzene instead of benzene established an analogous equilibrium mixture, but biased more in favor of the cyclometalated component 5. There is no incorporation of hydrogen into the benzene-d_6 solvent, and this demonstrates that the addition/elimination of the arene and alkyl C–H bonds to the metal center must be concerted processes. In solution, 5 must be in equilibrium with a reactive species such as 1[14,15] which can react in-

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[5] Lühder, K.; Nehls, D.; Madeja, K. *J. Prakt. Chem.* **1983**, *325*, 1027–9.

[6] Mays, M. J.; Prayter, B. E. *Inorg. Synth.* **1974**, *XV*, 21–5.

[7] ^{31}P NMR chemical shifts were measured at 162.0 MHz relative to external trimethyl phosphite (taken to be 141.18 ppm) at the temperature quoted. ^{13}C and ^{1}H NMR spectra were recorded at 100.0 and 400.1 MHz, respectively, and referenced to residual solvent absorptions. All chemical shifts are quoted with positive values to low field.

[8] Toluene-d_8 solution: δ(^{31}P) (228 K) 96.99 ($^{1}J_{\mathrm{PH}}$ = 43.2 Hz); δ(^{13}C) (215 K) FeCH$_3$, −21.39 ($^{1}J_{\mathrm{CH}}$ = 118.5 Hz, $^{2}J_{\mathrm{CP}}$ = 28.7 Hz); δ(^{1}H) (220 K) FeH, −18.93 ($^{2}J_{\mathrm{PH}}$ = 43.2 Hz), FeCH$_3$, −1.34 ($^{3}J_{\mathrm{PH}}$ = 5.7 Hz).

[9] Toluene-d_8 solution: δ(^{31}P) (242 K) 102.35, 99.16, 86.22, 74.64; δ(^{1}H) (238 K) FeH, −13.86, Fe–CH$_3$, −1.11.

[10] In dilute THF solution, 5 is relatively stable. On concentration or removal of the solvent, the material undergoes significant decomposition and has not been isolated in a pure form.

[11] Benzene-d_6 solution: δ(^{31}P) (298 K) 102.2 and 88.1 (exchange broadened); δ(^{1}H] −14.77 (exchange broadened multiplet, FeH) identical with that of an authentic sample prepared by reduction of Fe(DEPE)$_2$Cl$_2$ with LiAlH$_4$ in THF solution.

[12] Benzene solution: δ(^{31}P) (300 K) 91.01, 89.78, 76.23, 67.67 ppm. δ(^{1}H) −13.40 ppm (FeH).

[13] Benzene solution: δ(^{31}P) (300 K) 94.81; δ(^{1}H) −19.15 (FeH).

[14] Maldotti, A.; Sostero, S.; Traverso, O.; Sima, J. *Inorg. Chim. Acta* **1981**, *54*, L271–2. Azizian, H.; Morris, R. H. *Inorg. Chem.* **1983**, *22*, 6–9. Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Chem. Ber.* **1977**, *110*, 2200–12. Harris, T. V.; Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 6966–77. Creaser, C. S.; Kaska, W. C. *Inorg. Chim. Acta* **1978**, *30*, L325–6.

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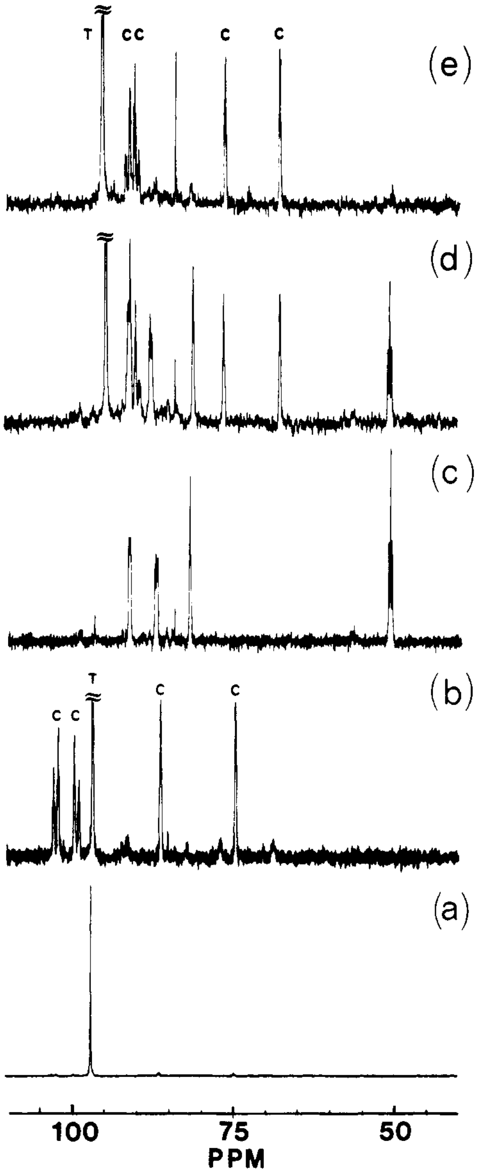

Figure 1. ^{31}P NMR spectra (162.0 MHz; proton decoupled). (a) *trans*-FeH(DEPE)$_2$Me (3) 228 K in toluene-d_8. (b) Mixture of *cis*- and *trans*-FeH(DEPE)$_2$Me obtained by warming the sample in Figure 1a to 240 K (toluene-d_8). Resonances of 3 labeled T, and resonances of 4 labeled C. (c) Spectrum of 5 (298 K· THF-d_8 solution). (d) Equilibrium mixture of 5, 6, and 7 (330 K; benzene). (e) Equilibrium mixture of 5, 6, and 7 (300 K; benzene). Resonances of 6 labeled C, and resonances of 7 labeled T.

termolecularly with a suitably "electron-rich" arene. The equilibrium, 1 ⇄ 5 is analogous to that proposed[16] to rationalise the reactions and infrared spectrum of Ru(DMPE)$_2$ [DMPE = 1,2-*bis*(diethylphosphino)ethane]. In the series of iron complexes described above, the close stability of 5, 6, and 7 balances the equilibrium so that all three complexes exist at comparable concentrations in the equilibrium mixture.

5 reacts intermolecularly with C–H bonds in naphthalene, toluene, and other organic compounds to yield alkyl and aryl iron hydrides in a manner similar to that reported[15] for the coordinatively unsaturated species Fe(DMPE)$_2$ generated from FeH(DMPE)$_2$Np [Np = 2-naphthyl].

Acknowledgment. We gratefully acknowledge financial support from the Australian Research Grants Scheme and the Australian Government for a Commonwealth Postgraduate Award (M.V.B.).

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[16] Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843–55.

A Catalytic Procedure for the Preparation of Carbonyl-Labeled Acyl Chlorides: More Mechanistic Insights into Decarbonylation Reactions Promoted by Rhodium(I) Complexes

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Summary: The reaction of RhCl(CO)(PPh$_3$)$_2$ with aliphatic acid chlorides in the presence of free ^{13}CO in CDCl$_3$ or C$_6$D$_6$ at 110 °C leads to catalytic incorporation of ^{13}CO. In this manner, carbonyl-labeled acetyl, phenylacetyl, butanoyl, octanoyl, 2-methylpropanoyl, 2-phenylpropanoyl, cyclopentanecarboxylic acid, and cyclohexanecarboxylic acid chlorides were prepared. Decarbonylation products, alkyl chloride or olefin, are not formed in significant yields and are not intermediates in the labeling process. Reductive elimination of alkyl chloride and β-hydrogen elimination of olefin from the intermediate organometallic complexes are slower, therefore, than the equilibration processes and reductive elimination of acid chloride that lead to CO exchange.

In previous publications we provided evidence for an interlocking set of organometallic intermediates in the reaction of RhCl(CO)(PPh$_3$)$_2$ (1) with aromatic acid chlorides at temperatures of the order of 100 °C (Scheme I).[1] The net equilibration, ArCOCl + RhCl(CO)(PPh$_3$)$_2$ $\rightleftharpoons$ 2CO + RhCl$_2$(Ar)(PPh$_3$)$_2$, provides a catalytic route to carbonyl-labeled aromatic acid chlorides by exchange with added ^{13}CO or with other carbonyl-labeled acid chlorides.[2] The reactions of the organometallic intermediates that lead to exchange must be faster than the formation of aryl chlorides from these intermediates, since aryl chlorides are not formed under the conditions of the equilibration.[2] It seemed clear from literature reports that the rate of formation of alkyl chlorides or olefins (by β-hydrogen elimination) is greater than the rate of formation of aryl chlorides in these systems.[3] Therefore, it was not obvious

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[1] Kampmeier, J. A.; Rodehorst, R. M.; Philip, J. B., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 1847–1849.

[2] Kampmeier, J. A.; Mahalingam, S. *Organometallics* **1984**, *3*, 489–491. It is important to emphasize that the equilibration proceeds in both the presence and the absence of added ^{13}CO. Aryl chloride is not formed in either case.[1] Added ^{13}CO, therefore, simply serves to reveal the equilibration reactions.